Combining fluorescence and phosphorescence to achieve very long lifetime, 100% efficient, high brightness white OLEDs

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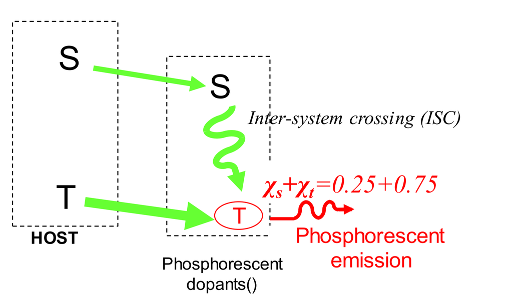
Background & Rationale

The efficiencies of monochromatic OLEDs have been pushed to near theoretical limits in both laboratory and commercial applications. This was done by efficiently harvesting that both singlet and triplet excitons formed on hole/electron recombination (ratio = 1:3). The prevalent solution to this harvesting problem is to use an emissive dopant in the OLED that has a heavy metal ion at its core to promote spin orbit coupling and thus efficient phosphorescence from the triplet .

Phosphorescent OLED



Pros:

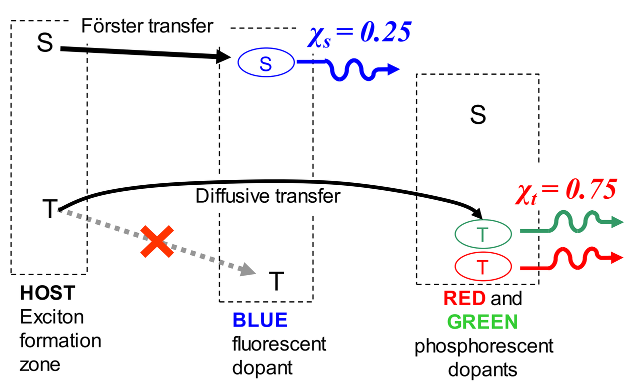
- High efficiency possible, up to 100%, and color tunable
- Low voltage, high lm/W possible

Cons:

- Emitter (color) mixing to achieve white can be complicated
- Lifetime of blue PHOLED is poor, limiting WOLED lifetime
- Exchange energy $S_1 \rightarrow T_1$ is lost, limiting power efficiency

In this research program we are focusing on an alternate solution that does NOT use phosphorescent dopants for all colors, but collects singlet excitons on a fluorescent dopant and triplets on one or more phosphorescent dopants. We first proposed this in 2006 (Y. Sun, *et. al*, *Nature*, **2006**, *440*, 908-912).

Hybrid fl/ph WOLED

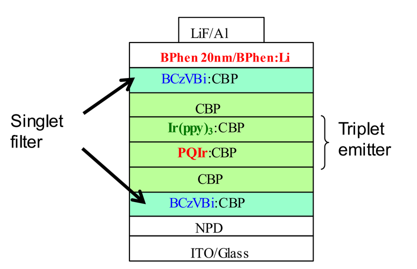


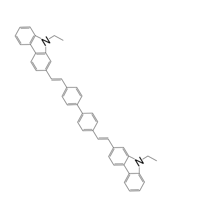
Pros:

- High efficiency possible, up to 100% for white
- Constant color with changing drive voltage
- Low voltage, high lm/W possible (no exchange energy loss)
- Blue from a fluorescent emitter, does not limit device lifetime

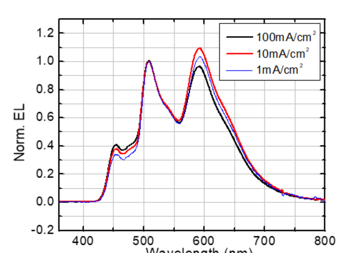
Cons:

- As pictured the triplet level of the fl-dopant is a trap
- Phosphorescent dopants can trap carriers: S_1:T_1 imbalance



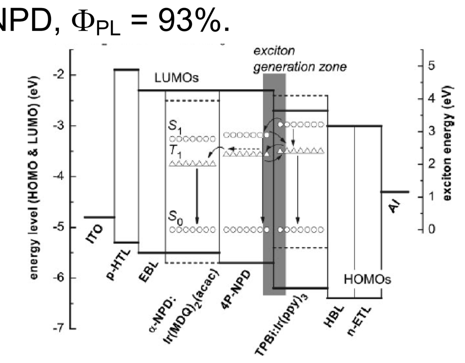


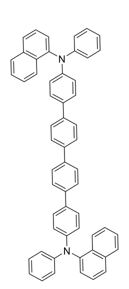
BCzVBi



Efficiency = 24 lm/W at 500 nits, CIE = (0.40, 0.41), CRI = 85, CCT = 3750K

Hybrid fl/ph WOLED with fluorescent Host: In 2007 Karl Leo introduced an alternate strategy in which a host matrix is used that fluoresces as a neat solid (Schwartz, G., *et. al. Adv. Mater.* **2007**, *19*, 3672). Singlet excitons are trapped near the interface (L_D ~ 10 nm). The host lattice used here was 4P-NPD, Φ_{PL} = 93%.





4P-NPD

Pros:

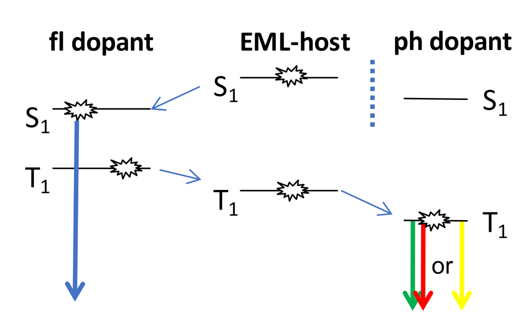
- Highly efficient fluorescence without doping
- Constant color with changing drive voltage
- Low voltage, high lm/W possible (no exchange energy loss)

Cons:

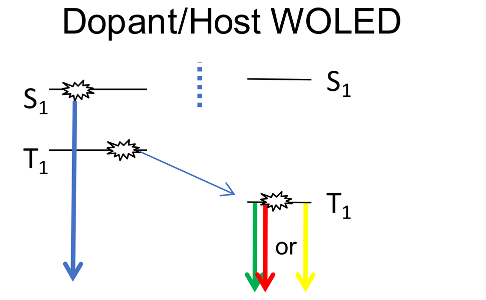
- Lifetime unknown (NPD emitter gives poor lifetime)

Our Objectives

1. Fluorescent emitters with small S_1/T_1 energy gaps
2. Host materials with wide S_1/T_1 energy gaps
3. Materials with strong blue fluorescence in the solid state (to act as a host material)
4. Investigate exciton diffusion in hybrids to maximize the efficiency of harvesting singlet and triplet excitons
5. Measure and optimize efficiencies and lifetimes of hybrid WOLEDs



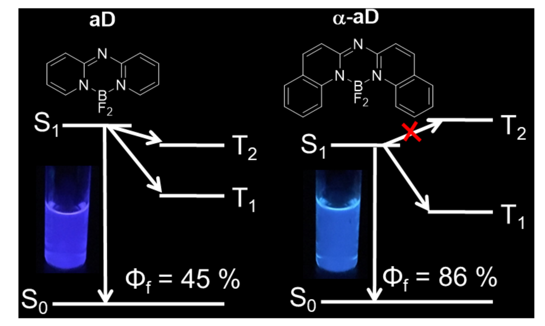
Dopant/Host WOLED



fl dopant is Host WOLED

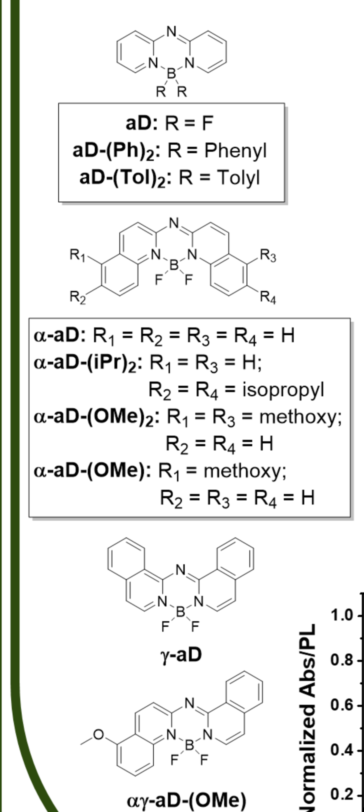
fl-dopants with small ΔE_{ST}

- Theory predicted aza-diquinomethanes would have **ΔE_{ST} < 0.4 eV**
- α-aD emitters have the expected low ΔE_{ST}
- The aza-DIPYR dopants fluoresce blue (λ_{max} < 470 nm) with high quantum efficiency (Φ = 45 % - 86 %) in solution and solid matrix
- Show high EL efficiency in CBP host and in potential hybrid host



Problems:

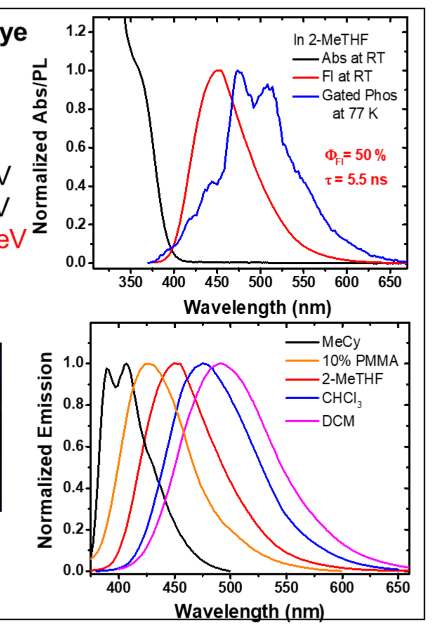
- T_1 energy is too low for CBP hosted hybrid
- HOMO levels of α-aD emitters are deep (> 6.0 eV), restricts hosts

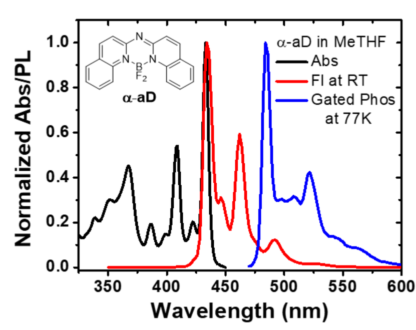


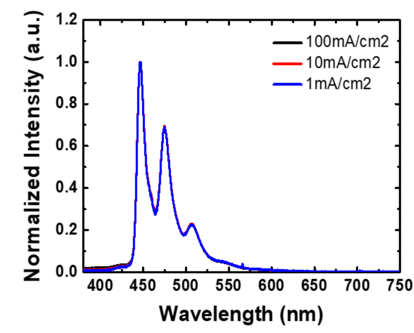
	S_1 (eV)	T_1 (eV)	$\Delta E(S_1/T_1)$	HOMO (eV)	LUMO (eV)	PLQY (%)
aD	3.11	2.64	0.47	-5.88	-2.06	42
aD-(Ph)$_2$	2.89	2.68	0.21	-5.62	-1.77	30
aD-(Tol)$_2$	2.82	-	-	-	-	-
α-aD	2.86	2.56	0.30	-6.21	-2.52	86
α-aD-(iPr)$_2$	2.79	2.51	0.28	-6.10	-2.44	87
α-aD-(OMe)$_2$	2.77	2.51	0.26	-5.92	-2.38	84
α-aD-(OMe)	2.81	2.53	0.28	-6.13	-2.33	84
γ-aD	2.87	2.57	0.28	-6.14	-2.31	87
αγ-aD-(OMe)	2.84	2.46	0.38	-6.06	-2.26	90

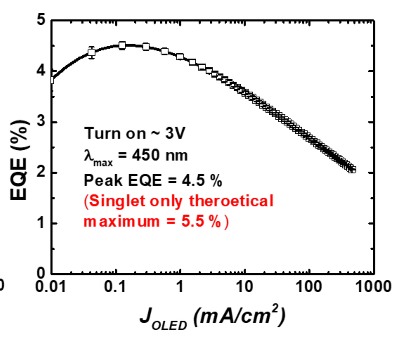
Coumarin Dye

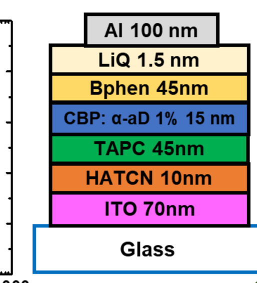
S_1 = 3.04 eV
T_1 = 2.65 eV
ΔE_{ST} < 0.4 eV







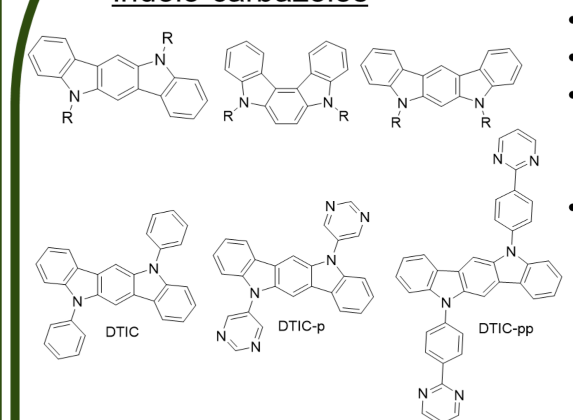




Host materials and fluorescent hosts

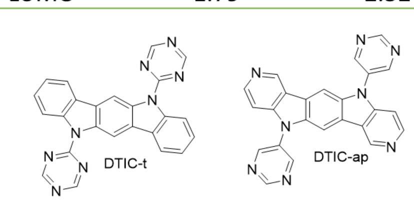
Host for fl-dopants

Indolo-carbazoles



- Appropriate S_1 and T_1 energies for **α-aD**
- 1 wt% film of **α-aD** in DTIC, DTIC-p, DTIC-pp
- Measured PLQY of the film < 4%
  - Exciplex quenching due to shallow HOMO of DTICs
- Synthesis of deep HOMO level materials in progress (DTIC-t and DTIC-ap)

	DTIC-p (eV)	α-aD (eV)
S_1	3.10	2.86
T_1	2.43	2.56
HOMO	-5.49	-6.21
LUMO	-1.79	-2.52



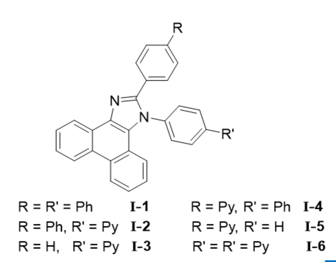
Blue Fluorescent Hosts

Phenanthro[9,10-*d*]imidazoles (**I-1 – I-6**)

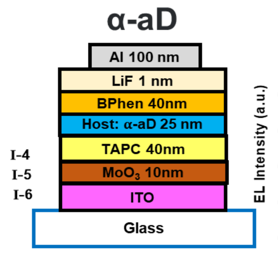
1. Tune energies using pyridine and phenyl moiety
2. Nest the energy levels and exciton energies of **α-aD**
3. PLQY of 1 wt% film of **α-aD** in all hosts **> 80%**
4. Blue fluorescence in the solid-state (**PLQY > 80%**)
5. Host yellow and red phosphorescent emitters with high efficiencies

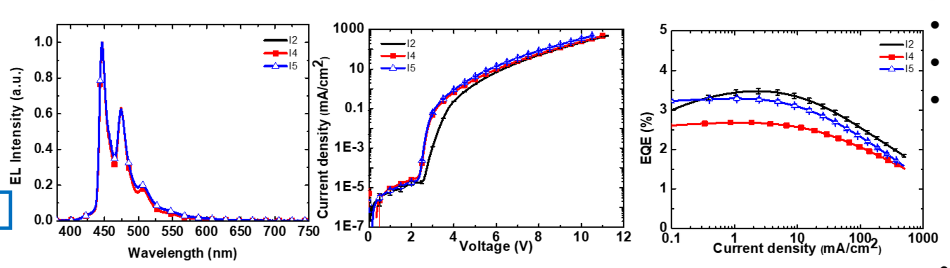
	S_1 (Soln)	S_1 (Solid)	T_1 (Soln)	T_1 (Solid)	HOMO (eV)	LUMO (eV)
I-1	373	377	441	468	-5.81	-1.70
I-2	375	382	477	490	-5.82	-1.89
I-3	365	370	460	478	-5.86	-1.89
I-4	390	412	478	520	-5.87	-2.03
I-5	390	406	480	520	-5.87	-2.00
I-6	386	410	475	495	-5.94	-2.00

S_1 and T_1 values are in nm

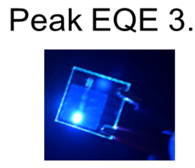


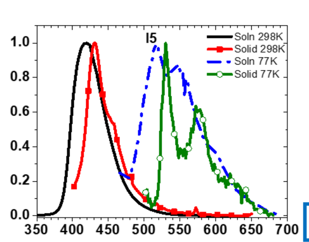
α-aD



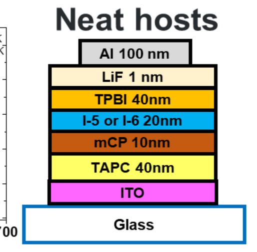


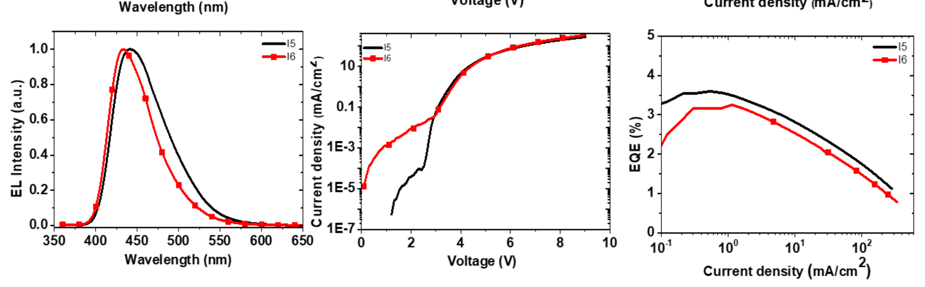
- λ_{max} = 450 nm
- Turn on ~ 3V
- Peak EQE 3.5%





Neat hosts

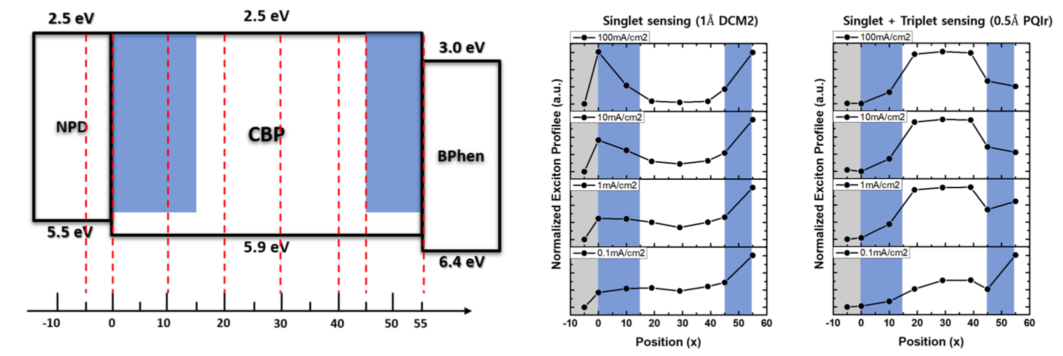




- λ_{max} = 440 nm
- Turn on ~ 3.2V
- Peak EQE 3.6%

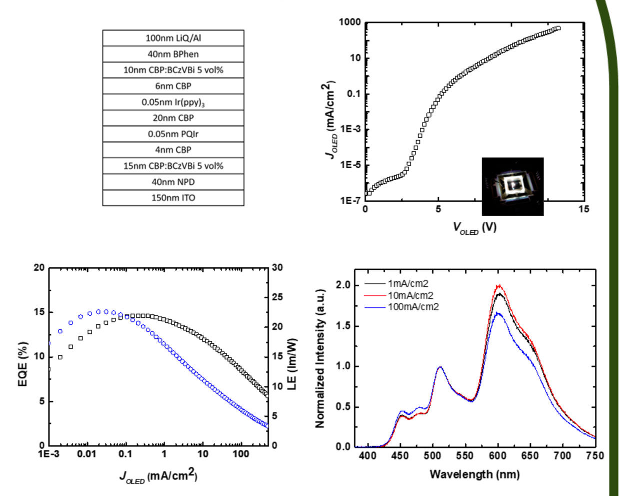
Hybrid WOLEDs

- Singlet/Triplet sensing of fl.ph hybrid device



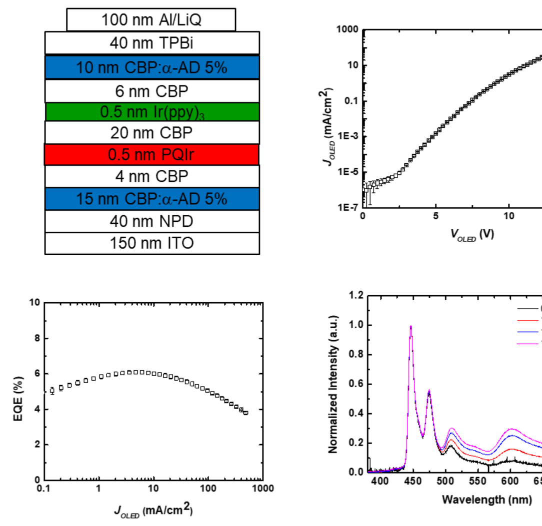
Exciton densities acquired using ultrathin "delta doped" sensing layers

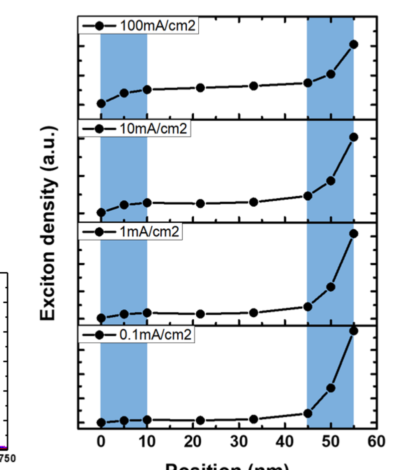
- Delta doped hybrid WOLED



Delta doping green and red works

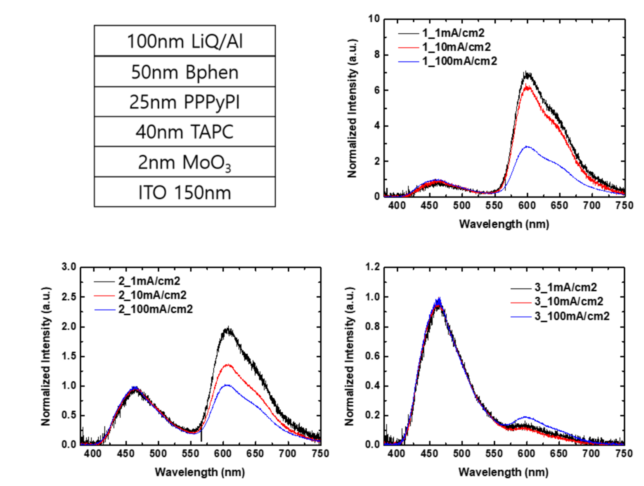
- α-aza DiPYR hybrid WOLED





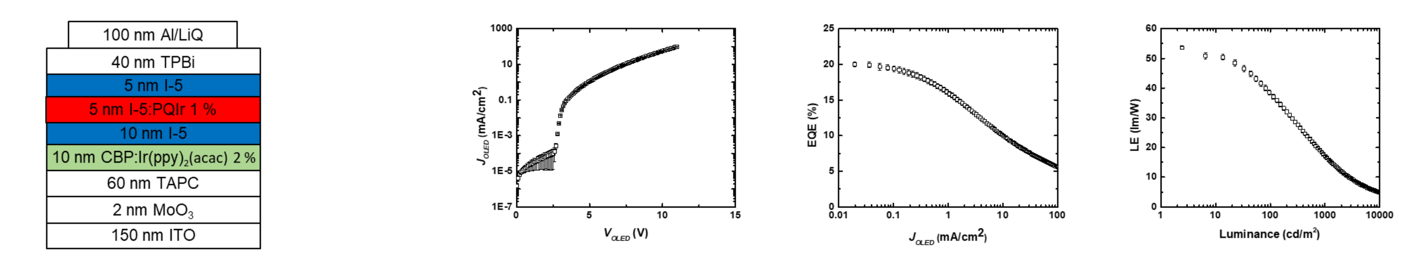
CBP triplets trapped at α-aza DiPYR sites

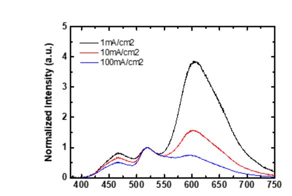
- I-5 (PPPyPI) sensing



Sensor positions:
D1 at 0nm, D2 at 17.5nm, D3 at 25nm
Exciton generation at anode side of EML

- I-5 hybrid WOLED

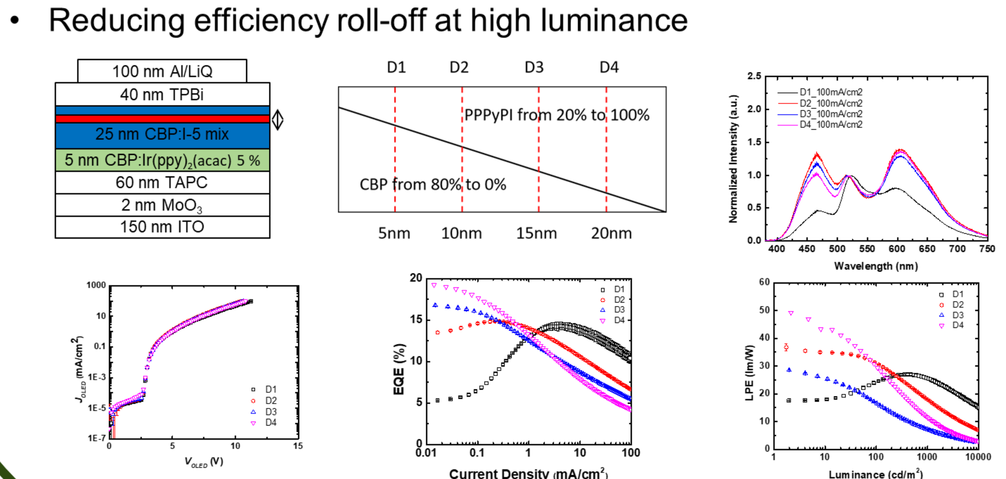




	CRI	CCT	CIE
1mA/cm²	74	2044	(0.5,0.38)
10mA/cm²	90	3170	(0.42,0.39)
100mA/cm²	83	4848	(0.35,0.42)

Peak power efficiency of 54.6lm/W and high CRI of 90 but rolls off extremely with increasing luminance

- Reducing efficiency roll-off at high luminance



Spreading exciton generation to relieve roll-off

D1 has higher power efficiency at high luminance compared to original device

More room for efficiency maximization
Currently losing triplets in EML

Acknowledgements

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U.S. DEPARTMENT OF ENERGY
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